English Language Machine Translation JP 06-027215 B

Notes:
1. Untranslatable words are replaced with asterisks (****).
2. Texts in the figures are not translated and shown as it is.

Translated: 21:49:12 JST 06/18/2008
Dictionary: Last updated 05/30/2008 / Priority: 1. Chemistry

CLAIM + DETAILED DESCRIPTION

[Claim(s)]
[Claim 1] The manufacture method of the hydrophilic polyvinylidene fluoride porous membrane which carries out a chemical treatment in the strong alkali solution containing an oxidizing agent, and is characterized by immersing this porous membrane further into the compound solution which has a hydrophilic group after creating the porous membrane which consists of polyvinylidene fluoride and infiltrating a basin system solvent into the pore part of this porous membrane.
[Claim 2] The manufacture method of a hydrophilic polyvinylidene fluoride porous membrane given in the 1st clause of the range of the application for patent whose oxidizing agent is potassium permanganate.
[Claim 3] The manufacture method of a hydrophilic polyvinylidene fluoride porous membrane given in the 1st clause of the range of the application for patent which is the aqueous solution in which a strong alkali solution dissolves potassium hydroxide or sodium hydroxide.
[Claim 4] The manufacture method of a hydrophilic polyvinylidene fluoride porous membrane given in the 1st clause of the range of the application for patent whose compound solution which has a hydrophilic group is a solution of the compound which has the hydrophilic group of 1% or more of moisture absorption in the atmosphere of 50% of relative humidity.
[Claim 5] The compound which it has a hydrophilic group Hydroxyethyl cellulose, hydroxypropylcellulose, A hydrophilic polyvinylidene fluoride porous membrane given in either the 1st clause of the range of the application for patent chosen from the group which consists of polyvinyl pyrrolidone, polyethylene glycol, and carboxymethylcellulose - the 4th clause.
[Claim 6] A hydrophilic polyvinylidene fluoride porous membrane given in either the 1st clause of the range of the application for patent whose compound which has a hydrophilic group is collagen or denaturation collagen - the 4th clause.
[Claim 7] A hydrophilic polyvinylidene fluoride porous membrane given in either the 1st clause of the range of the application for patent whose compound which has a hydrophilic group is a compound which has surface activity - the 4th clause.
[Claim 8] A hydrophilic polyvinylidene fluoride porous membrane given in either [as which the compound which has a hydrophilic group is chosen from the group which

consists of glycerol, a monosaccharide, an oligosaccharide, an amino acid, and oligopeptide] the 1st clause of the range of an application for patent - the 4th clause.
[Claim 9] The manufacture method of the hydrophilic polyvinylidene fluoride porous membrane which carries out a chemical treatment in the strong alkali solution containing an oxidizing agent, and is characterized by immersing this porous membrane further into the compound solution which has a hydrophilic group after creating the porous membrane which consists of polyvinylidene fluoride and infiltrating a basin system solvent into the pore part of this porous membrane.
[Claim 10] The manufacture method of a hydrophilic polyvinylidene fluoride porous membrane given in the 9th clause of the range of the application for patent whose oxidizing agent is potassium permanganate.
[Claim 11] The manufacture method of a hydrophilic polyvinylidene fluoride porous membrane given in the 9th clause of the range of the application for patent which is the aqueous solution in which a strong alkali solution dissolves potassium hydroxide or sodium hydroxide.
[Claim 12] The manufacture method of a hydrophilic polyvinylidene fluoride porous membrane given in the 9th clause of the range of the application for patent whose compound solution which has a hydrophilic group is a solution of the compound which has the hydrophilic group of 1% or more of moisture absorption in the atmosphere of 50% of relative humidity.

[Detailed Description of the Invention]
(Field of the Invention)
This invention relates to the manufacture method of a hydrophilic polyvinylidene fluoride porous membrane. If it states in detail, hydrophilization of this invention will be carried out completely uniformly, and it will aim at offering the manufacture method of the hydrophilic high polyvinylidene fluoride porous membrane of gamma ray-proof nature and chemical resistance.
(PRIOR ART)
The porous membrane of the cellulosic which has high water permeability conventionally as a hydrophilic porous membrane used for various kinds of ** faults, a dialysis, etc., especially cellulose acetate was common. However, when the resistance over a gamma ray needed [in / it is low and / a medical field] gamma ray sterilization, such a cellulosic could not be used and was inferior in respect of the resistance over medicine, such as an acid, an alkali, and an organic solvent, and the operating condition was what is limited sharply.
Although the porous membrane excellent in chemical resistance made from the polyvinylidene fluoride which is fluorine system polymer, tetrafluoroethylene, etc. as what is replaced with the porous membrane of these cellulosics, and gamma ray resistance was developed Since it is a hydrophobic porous membrane, in order to use it as a demarcation membrane in the solution of a basin system, "hydrophilization" of these needed to be carried out.
As the hydrophilization treatment method of such a hydrophobic porous membrane, the method of coating the pore surface with the chemical modification method and surface active agent on the surface of a pore of a porous membrane is known conventionally.

However, the present condition is that the practical chemical treatment method is not established about the former method since it is special form, such as that the chemical resistance of polyvinylidene fluoride is high, and a porous membrane. The defluorination acid of the polyvinylidene fluoride is carried out in the strong alkali solution of potassium hydroxide and sodium hydroxide. To intramolecular a double bond mainly It produces and bronzing or black-izing are known (a journal OBU polymer science, polymer chemistry edition [J. Polym.Sci. and Polym.Chem.Ed.] 21, 3443-3451 (1983)). Although carrying out hydrophilization of the polyvinylidene fluoride including this bronzing or black-ized double bond by carrying out vitriolization is also considered (the collection of Japanese Society of Polymer Science, Japan drafts the 33rd volume, No. 3 (1984)). By this method, it had the fatal fault that only the porous membrane which hardness fell remarkably by the oxidative degradation of the principal chain, and was colored brown was obtained. Moreover, [after carrying out a defluorination acid in a strong alkali solution, how to introduce a polar group into a double bond by oxidation treatment is also considered, but] By this method, the process was what the problem of bronzing of the film by a strong remarkable fall and the double bond which remains further produces on the conditions which carry out hydrophilization of the pore surface of about [that become two processes and operation becomes complicated] and a porous membrane completely. Since a processed material has the special form of a "porous membrane", these problems are generated. Namely, the double bond generated inside when the chemical treatment was strengthened and having been processed even inside the base material becomes is hard to be processed by oxidation treatment in the 2nd process. It is because things become impossible when that to which hydrophilization of the porous membrane was carried out uniformly completely will not become if a film bronzes, physical properties also fall and a chemical treatment is weakened on the other hand, but the purpose is attained.

Moreover, although simple treatment could give hydrophilic nature about the latter method, there was a problem that the coated surface active agent was eluted, and it was not desirable from the field of "safety" on the occasion of the use especially in food and a medical field.

Although how to coat glycerol with high safety or a part of hydrophilic polymer to a human body furthermore is also known Since the hydrophobicity of polyvinylidene fluoride was high, a porous membrane could not be coated uniformly and a hydrophilic polyvinylidene fluoride porous membrane was not able to be obtained.

(Problem which invention tends to solve)

Therefore, this invention aims at offering the manufacture method of a new hydrophilic polyvinylidene fluoride porous membrane. Hydrophilization of this invention is carried out completely uniformly, and it aims at offering the manufacture method that the hydrophilic high polyvinylidene fluoride porous membrane of gamma ray-proof nature and chemical resistance can be obtained again. This invention aims at offering the manufacture method that it excels still in appearance and the hydrophilic high polyvinylidene fluoride porous membrane of a brand image can be obtained. This invention aims at offering the method of manufacturing a hydrophilic polyvinylidene fluoride porous membrane still more easily and quickly.

(Means for solving a problem)

Many above-mentioned purposes create the porous membrane which consists of

polyvinylidene fluoride again. After infiltrating a basin system solvent into the pore part of this porous membrane, it is attained by the manufacture method of the hydrophilic polyvinylidene fluoride porous membrane which carries out a chemical treatment in the strong alkali solution containing an oxidizing agent, and is characterized by immersing this porous membrane further into the solution of the compound which has a hydrophilic group.

This invention shows the manufacture method of a hydrophilic polyvinylidene fluoride porous membrane that an oxidizing agent is potassium permanganate again. This invention shows further the manufacture method of the hydrophilic polyvinylidene fluoride porous membrane which is an aqueous solution that a strong alkali solution dissolves potassium hydroxide or sodium hydroxide. This invention shows the manufacture method of a hydrophilic polyvinylidene fluoride porous membrane which is the solution of a compound that the compound solution which has a hydrophilic group again has the hydrophilic group of 1% or more of moisture absorption in the atmosphere of 50% of relative humidity.

"Porous membrane [hydrophilic]" In addition, into this Description, waterdrop sinks into the inside of a porous membrane by prudence, and the becoming term is used as what means the porous membrane which can also wet the surface by the side of opposite, and by which hydrophilization was carried out highly, when waterdrop is dropped on a porous membrane.

(OPERATION)

[the hydrophilic polyvinylidene fluoride porous membrane obtained by the manufacture method of this invention] Since the compound which has a hydrophilic group is made to stick to the hydrophilization layer which the polar group was introduced and was formed on the polyvinylidene fluoride molecule which is a base material and hydrophilization treatment only of the pore surface is moreover carried out to it The stable hydrophilic nature without aging is shown, and since it is possible to make thin thickness of the hydrophilization layer in which a polar group is made to introduce and form, the outstanding physical properties which polyvinylidene fluoride has can be enjoyed, and it becomes the outstanding hydrophilic polyvinylidene fluoride porous membrane of gamma ray-proof nature and chemical resistance.

In the manufacture method of the hydrophilic polyvinylidene fluoride porous membrane of this invention, by carrying out a chemical treatment in the strong alkali solution which contains an oxidizing agent first, a polar group is introduced on a polyvinylidene fluoride molecule, and a hydrophilization layer is formed in the pore surface. Since [thus,] the double bond generated to polyvinylidene fluoride by the defluorination acid reaction by operation of strong alkali is oxidized in an instant and a polar group can be introduced, when an oxidizing agent is made to act in a strong alkali solution It is thought that there is no coloring of the film which is not made to generate a superfluous double bond and **** to this double bond, and it is equal in any way also in appearance compared with an unsettled polyvinylidene fluoride porous membrane. Therefore, it can be considered as the hydrophilic porous membrane which showed sufficient hydrophilic nature and was excellent also in other characteristics only by introducing a polar group on a polyvinylidene fluoride molecule, and forming a hydrophilization layer in the pore surface by carrying out a chemical treatment in the strong alkali solution which contains an oxidizing agent in this way. However, the hydrophilic nature which introduced the

polar group into the surface of the hydrophobic polymer membrane, and was given to it may be lost often temporally. [this] for example, journal OBU Polymer A science and polymer Physics Edition 19 and 1285(1981) [-- J. -- Polym.Sci., Polym.Phys.Ed.19, 1285(1981)], and journal OBU Applied Polymer Science 29 4335-4340(1984) [J. as indicated to Appl.Polym.Sci.29 4335-4340(1984)] It is thought that it is because a polar group will move to the inside of a molecule and the surface will be again covered with a hydrophobic polymer, and this cause is considered with since the direction of the small hydrophobic surface of surface free energy is in a more stable existence state in the interface of the polymer surface and air. In order to prevent such a temporal change, how to thicken a surface hydrophilization layer can be considered, but by this method, the problem of the case "a fall of physical properties (hardness)" of a "porous membrane" is produced.

In the manufacture method of the hydrophilic polyvinylidene fluoride porous membrane of this invention After introducing a polar group on a polyvinylidene fluoride molecule and forming a hydrophilization layer in the pore surface by carrying out a chemical treatment in consideration of the problem like the above in the strong alkali solution containing an oxidizing agent, Treatment which makes the compound which immerses this porous membrane into the solution of the compound which has a hydrophilic group, and has a hydrophilic group stick to this hydrophilization layer is performed. [the pore surface of a polyvinylidene fluoride porous membrane] Since it has the hydrophilization layer formed by introducing a polar group, it adsorbs very good and the compound which has the hydrophilic group with which an unsettled polyvinylidene fluoride porous membrane cannot be adsorbed or coated forms a uniform film in the pore surface. [thus, the hydrophilic polyvinylidene fluoride porous membrane of this invention obtained] Since the hydrophilization layer on the surface of a pore is stabilized using the moisturizing effect based on the polar group of a compound and hygroscopic property which have the hydrophilic group by which the pore surface was mainly adsorbed [the hydrophilization layer in which a polar group is made to introduce and form first] [that what is necessary is just to have the function which keeps good adsorbent / of the compound which has a hydrophilic group at least] It can be given without spoiling the physical properties which were excellent in polyvinylidene fluoride, as it becomes possible to make it thin and the thickness of this hydrophilization layer was described above, and becomes the hydrophilic porous membrane which shows the physical properties which were excellent in addition to having the stable hydrophilic nature without temporal change.

This invention is hereafter explained in detail based on an embodiment.

In the manufacture method of the hydrophilic polyvinylidene fluoride porous membrane of this invention As polyvinylidene fluoride which constitutes the hydrophobic porous membrane used as a base material, copolymers which made the subject vinylidene fluoride other than a vinylidene fluoride homopolymer, such as tetrafluoroethylene, methyl acrylate, methyl methacrylate, and propylene, may also be used.

[the porous membrane which consists of such polyvinylidene fluoride] Although it may be prepared by a well-known method, resin is dissolved in a solvent. After spreading in predetermined form and evaporating some solvents, it is immersed into a solvent and the non solvent which has miscibility, and a solvent is extracted. It mixture-solution-spreads in desired form by using the wet method which a non solvent and a residual solvent are

evaporated completely after that, and obtains a porous membrane, or resin as the non solvent which can mix with a solvent and a solvent from the beginning, and is prepared by the dry process which a solvent and a non solvent are evaporated completely and obtains a porous membrane. Desirably [a polyvinylidene fluoride porous membrane] It sets using the mixture of the quick-drying solvent and slow-drying solvent which differ in a steamy partial pressure as a solvent used in a steamy wet method or a dry process as shown in a JP,49-126,572,A number and a JP,52-154,862,A number at the time of gelling. With this slow-drying solvent, in part, the dissolution or nothing [a swelling state and nothing], and mechanical hardness are raised, and resin is prepared. As for 100-200 micrometers and 0.1-1.0 micrometers of average pore sizes, the porous membrane of hydrophobic polymer is preferably prepared [50-300 micrometers of usual thickness] by the 0.2-0.6-micrometer thing by such a method.

The porous membrane which consists of prepared hydrophobic polyvinylidene fluoride has it made like the above in the manufacture method of this invention to infiltrate a basin system solvent into the pore part first.

It can perform infiltrating a basin system solvent into the pore part of the porous membrane which consists of hydrophobic polyvinylidene fluoride by a well-known method, for example, an organic solvent-water substitution method, the method of infiltrating a basin system solvent, after coating a surface active agent, etc. are used. An organic solvent-water substitution method is performed to the organic solvent which has the water and miscibility like an alcohol, such as ethanol, at first by replacing a solvent by the organic solvent-water mixed solution series which immerses a polyvinylidene fluoride porous membrane, then has a concentration gradient one by one, and finally replacing by water.

Thus, the chemical treatment of the polyvinylidene fluoride porous membrane which infiltrated the basin system solvent into the pore part is carried out in the strong alkali solution which contains an oxidizing agent next, and a hydrophilization layer is formed in the pore surface.

In the manufacture method of this invention in order to make the oxidizing agent intermingled in a strong alkali solution in this way It is thought that the double bond which the defluorination acid was carried out by the operation of strong alkali on the surface of the immersed polyvinylidene fluoride porous membrane, and was generated to intramolecular can oxidize by an oxidizing agent immediately, and can introduce a polar group, and there is no generation of this, therefore a superfluous double bond.

As a strong alkali solution used in the manufacture method of this invention Although the alkali solution containing potassium alkoxide, such as sodium alcoholate, such as sodium methoxide and sodium ethoxide, or potassium methoxide, potassium ethoxide, and potassium isopropoxide, etc. is used To be the aqueous solution which dissolved potassium hydroxide and sodium hydroxide is more preferably desired from when preventing maintenance of the physical properties of a porous membrane, the formation of a covering color (depth of a chemical treatment layer), and oxidation of a solvent itself [by the oxidizing agent to contain]. Moreover, concentration of such an alkali solution is more preferably made into about 25 to 35 weight % ten to 40weight %.

Although various oxidizing agents, such as inorganic acid-ized agents, such as chromates and permanganate, and organic peroxide, are used as an oxidizing agent contained in such a strong alkali solution on the other hand from fields, such as economical efficiency

and operativity, -- desirable -- permanganate -- it is potassium permanganate most preferably. Although the amount of addition of the oxidizing agent to the inside of the above-mentioned strong alkali solution changes also with the kinds of oxidizing agent, it is about 4 to 8 weight % more preferably two to 10weight %.
Moreover, you may add layer move catalysts, such as a catalyst, for example, t-butyl ammonium star's picture etc., in the strong alkali solution containing this oxidizing agent. As processing time in the inside of the strong alkali solution containing such an oxidizing agent in the manufacture method of this invention Although it is influenced by an oxidizing agent and the concentration of an alkali compound, and treatment solution temperature and cannot generally crawl, hydrophilization layer usually sufficient by being immersed preferably for 3 to 8 minutes for 1 minute - 60 minutes is formed, and the physical properties of a polyvinylidene fluoride porous membrane are not fallen. Moreover, 20-100 degrees C of temperature of a treatment solution shall be about 60-90 degrees C more preferably.
After forming a hydrophilization layer in the pore surface of a porous membrane by introducing a polar group in this way, the compound which has a hydrophilic group in this hydrophilization layer is made to adsorb in the manufacture method of this invention by immersing this porous membrane into the compound solution which has a hydrophilic group. in addition, treatment liquid, manganese dioxide, etc. which preceded being immersed into the compound solution which has a hydrophilic group, and have adhered to the film after the above-mentioned chemical treatment -- 0.01-10 -- it is desirable to fully be more preferably washed with 1 w/v% of the sulfuric acid acidic solution and water of sodium hydrogensulfite w/v%.
As a compound which has the hydrophilic group used in the manufacture method of this invention in order to make it stick to the above-mentioned hydrophilization layer If it has sufficient hydrophilic nature, although any are sufficient, desirably It is desirable that it is 1% or more of moisture absorption in the atmosphere of 50% of relative humidity, and, specifically, hydrophilic polymers, such as hydroxyethyl cellulose, hydroxypropylcellulose, polyvinyl pyrrolidone, polyethylene glycol, and carboxymethylcellulose, are mentioned. Moreover, in using the hydrophilic polyvinylidene fluoride porous membrane of this invention for uses, such as a cell culture, while giving the outstanding hydrophilic nature, it can raise adhesion and fecundity of a cell remarkably by using collagen or denaturation collagen as a compound which has a hydrophilic group. Although the compound which has surface activity like various anionic surfactants, a cationic surfactant, both the ion surface active agent, and a nonionic surface active agent as a compound which furthermore has a hydrophilic group, for example, and compounds, such as glycerol, a monosaccharide, an oligosaccharide, and an amino acid, are used Of course, it is not necessarily limited to these.
The porous membrane which had the hydrophilization layer formed the compound which has such a hydrophilic group A suitable solvent, using a basin system solvent preferably -- 0.05-2.0 -- it is preferably immersed in the solution which dissolves in about [0.1-0.5 w/v%] concentration more preferably for 1 to 5 minutes w/v% for 0.2 to 30 minutes, and you are made to adsorb the compound which has a hydrophilic group in a hydrophilization layer After the end of immersion treatment, the film of the compound which desiccation treatment for 2 to 30 minutes is performed by desiccation treatment, for example, 60-110 degrees C, is removed in a solvent, and has a hydrophilic group on

the pore surface is formed, and a porous membrane serves as a product. In addition, after immersion treatment, in order to remove the compound which has a superfluous hydrophilic group adhering to a porous membrane, you may wash with water.
[the hydrophilic polyvinylidene fluoride porous membrane 1 obtained as mentioned above] Property modification only of the porous surface part of the base material 2 which consists of a polyvinylidene fluoride porous membrane as typically shown in Fig. 1 is carried out in the hydrophilization layer 3 into which the polar group was introduced uniformly. The uniform hydrophilic coating 4 to which the compound which furthermore has a hydrophilic group to this hydrophilization layer 3 sticks is formed. Since hydrophilic nature is raised and it is made to stabilize also temporally by making the compound which has a hydrophilic group in the hydrophilization layer 3 on the surface of a pore adsorb, while good hydrophilic nature is shown Since this hydrophilization layer 3 can be designed thinly, many outstanding physical properties which polyvinylidene fluoride originally has, such as chemical resistance and gamma ray resistance, are enjoyed highly. Furthermore, it sets to the hydrophilic polyvinylidene fluoride porous membrane 1 concerning this invention. There is also no possibility of bronzing from a superfluous double bond not existing in the hydrophilization layer 3 formed by introducing a polar group. In a dry state, it is, and it carries out, and assumes colorlessness, and the hydrophilic polyvinylidene fluoride porous membrane 1 concerning this, therefore this invention does not have a polyvinylidene fluoride porous membrane with an unsettled white reflection spectrum in the visible region, and an in any way change. [moreover, the hydrophilic polyvinylidene fluoride porous membrane 1 concerning this invention] Since it has the film 4 to which the compound which has a hydrophilic group to the hydrophilization layer 3 formed by introducing a polar group sticks [the state, i.e. the state of having only the hydrophilization layer 3 formed by introducing a polar group, where the compound whose hydrophilic nature of the also improves and which has a hydrophilic group is not adsorbing] The perviscosity which cannot invade in a pore, and a high-concentration solution, for example, a 30 w/v% grape sugar solution, enable it to invade in the pore of the hydrophilic polyvinylidene fluoride porous membrane 1, and the hydrophilic nature stabilized also temporally is held.
Although the hydrophilic polyvinylidene fluoride porous membrane concerning this invention is used in the field of the versatility because of the outstanding chemical resistance, gamma ray-proof nature, water permeability, ** fault efficiency, and mechanical hardness As main examples of a use, there are films for artificial organs, such as a final filter for a drug solution and infusion solutions and a medicine manufacture filter, an artificial kidney, and plasma separation, etc.
Next, a concrete operation of the hydrophilic polyvinylidene fluoride porous membrane of this invention is explained taking the case of the case of an infusion solution final filter.
The final filter 7 incorporating the hydrophilic polyvinylidene fluoride porous membrane 1 concerning this invention is sterilized and attached in the middle of the infusion solution inner tube 6 which is open for free passage to the infusion solution bag 5 as shown in Fig. 2 . An infusion solution is dropped at a final filter 7 through the infusion solution inner tube 6 from the infusion solution bag 5. It is caught by the hydrophilic polyvinylidene fluoride porous membrane 1 of a final filter 7, only the normalized infusion solution passes a final filter 7, and a fungus, bacteria, particles, etc. which were

mixed into the infusion solution here are sent in into a patient's 9 vein from the pouring needle 8 through the infusion solution inner tube 6. Therefore, the complication resulting from a fungus, bacteria, particles, etc. which were mixed into the infusion solution is prevented.

(EXAMPLE)

A work example explains this invention still more concretely hereafter.

[a work-example 1 polyvinylidene-fluoride powder (Mitsubishi Petrochemical Co., Ltd. make, Kynar K301) 18 weight part] [the solution which dissolves in an acetone 73.8 weight part and a dimethylformamide 8.2 weight part] After carrying out the cast on a polyethylene terephthalate film, it was immersed for 5 minutes during 1, 1, and 1-bird chloro 2 and 2 and 2-trifluoro ethane bath, and it dried and 150 micrometers of thickness and the hydrophobic polyvinylidene fluoride porous membrane of 0.45 micrometer of average pore sizes were obtained.

Thus, after the obtained hydrophobic polyvinylidene fluoride porous membrane was immersed in an ethanol aqueous solution 70%, water displacement was carried out by being immersed in distillation underwater, and water was infiltrated into the pore part. Next, this porous membrane was immersed for 5 minutes at 80 degrees C into the solution which dissolves potassium permanganate of 5 weight parts, and potassium hydroxide of 28 weight parts in a water 67 weight part, and the chemical treatment was performed. After taking out a film, the sulfuric acid acidic solution of water and 1 w/v% sodium hydrogensulfite fully washed the treatment liquid and manganese dioxide adhering to a film. Thus, after forming a hydrophilization layer in the pore surface of a porous membrane, and this porous membrane is immersed in a 0.5 w/v% polyvinyl pyrrolidone (made in [Tokyo Chemicals], molecular weight 40,000) aqueous solution for 5 minutes, picking takes out. Washed for 30 seconds, it was made to dry in oven (60 degrees C, 2 hours), and the hydrophilic polyvinylidene fluoride porous membrane was obtained.

Thus, in order to investigate the hydrophilic nature of the obtained hydrophilic polyvinylidene fluoride porous membrane, distilled water and a 30 w/v% grape sugar solution were dropped on this porous membrane. It became clear that in the case of which invade into a membranous pore part in an instant, and sufficient hydrophilic nature is given as shown in the 1st table as a result. The place which furthermore neglected this porous membrane for one month in the desiccator, and observed change of temporal hydrophilic nature, As shown in the 1st table, both distilled water and a 30 w/v% grape sugar solution invaded into the membranous pore part also even after one-month progress in an instant, and it became clear that the temporal fall of hydrophilic nature is not seen, either.

Moreover, the obtained hydrophilic polyvinylidene fluoride porous membrane had white appearance, and it was the same as that of the hydrophobic polyvinylidene fluoride porous membrane before a chemical treatment (unsettled thing). [of it] The result of furthermore having measured the reflection spectrum in the 370-700nm visible region of a hydrophilic polyvinylidene fluoride porous membrane using the reflective spectrophotometer (made in Shimazu, TLC SCANNER CS-930), As shown in Fig. 3 , it became the completely same spectrum pattern as the thing of the hydrophobic polyvinylidene fluoride porous membrane before a chemical treatment.

The hydrophilic polyvinylidene fluoride porous membrane was obtained like the work

example 1 except replacing with a work-example 20.5 w/v% polyvinyl pyrrolidone aqueous solution, and using a 0.5 w/v% hydroxypropylcellulose (Nippon Soda Co., Ltd. make, HPC-L) aqueous solution. When the hydrophilic nature of the obtained hydrophilic polyvinylidene fluoride porous membrane was investigated like the work example 1, as shown in the 1st table, good hydrophilic nature was shown like the thing of a work example 1, and temporal deterioration was not seen, either.

The hydrophilic polyvinylidene fluoride porous membrane was obtained like the work example 1 except replacing with a work-example 30.5 w/v% polyvinyl pyrrolidone aqueous solution, and using a polyethylene glycol (Nakarai Chemical, Ltd. make, molecular weight 20,000) aqueous solution. When the hydrophilic nature of the obtained hydrophilic polyvinylidene fluoride porous membrane was investigated like the work example 1, as shown in the 1st table, good hydrophilic nature was shown like the thing of a work example 1, and temporal deterioration was not seen, either.

The hydrophobic polyvinylidene fluoride porous membrane was created like comparative example 1 work example 1, it processed with the strong alkali solution containing an oxidizing agent, and the polyvinylidene fluoride porous membrane which has a hydrophilization layer on the pore surface was obtained. When the hydrophilic nature of this porous membrane was investigated like the work example 1, as shown in the 1st table, distilled water invaded into the pore part of the porous membrane in an instant, but the 30 w/v% grape sugar aqueous solution did not invade into a pore part within 20 seconds, but that hydrophilic nature was what a little inferior. The permeability of the distilled water after one more month progress was a little inferior, and temporal change was accepted.

Although the compound which processes with the compound solution which has a hydrophilic group like work examples 1-3, and has a hydrophilic group was made to adsorb and being tried as like, without processing with the strong alkali solution which creates a hydrophobic polyvinylidene fluoride porous membrane like two to comparative example 4 work example 1, and contains an oxidizing agent after that The compound which carries out a hydrophilic group owner was not adsorbed, and as shown in the 1st table, it was not able to give hydrophilic nature to a porous membrane.

As opposed to the cellulose acetate porous membrane (Millipore Corp. make and HAWP 14200 lot number N2J50023A, 0.45 micrometer of average pore sizes) of comparative example 5 marketing Work example 1 When hydrophilic nature was investigated similarly, as shown in the 1st table, the 30 w/v% grape sugar solution did not invade into a pore part within 30 seconds.

The place which measured the reflection spectrum in the 370-700nm visible region of the hydrophilic polyvinylidene fluoride porous membrane (Millipore Corp. make and IPKG GVWP 29325 lot number C6E04877) of comparative example 6 marketing like the work example 1, As shown in Fig. 3 , absorption of the spectrum in a low wavelength field serves as size, and it was colored light brown in appearance and clearly.

It replaces with a work-example 40.5 w/v% polyvinyl pyrrolidone aqueous solution, and is 1 w/v% polyoxyethylene. The hydrophilic polyvinylidene fluoride porous membrane was obtained by a work example 1 and Hitoshi except using a polyoxypropylene copolymer (product [made from Asahi Electrification], Pluronic F-68) solution. When the hydrophilic nature of the obtained hydrophilic polyvinylidene fluoride porous membrane was investigated like the work example 1, as shown in the 1st table, good

hydrophilic nature was shown like the thing of a work example 1, and temporal deterioration was not seen, either.

The hydrophilic polyvinylidene fluoride porous membrane was obtained like the work example 1 except replacing with a work-example 50.5 w/v% polyvinyl pyrrolidone aqueous solution, and using a 5 w/v% glycerol aqueous solution. When the hydrophilic nature of the obtained hydrophilic polyvinylidene fluoride porous membrane was investigated like the work example 1, as shown in the 1st table, good hydrophilic nature was shown like the thing of a work example 1, and temporal deterioration was not seen, either.

The hydrophilic polyvinylidene fluoride porous membrane was obtained like the work example 1 except replacing with a work-example 60.5 w/v% polyvinyl pyrrolidone aqueous solution, and using a 5 w/v% grape sugar aqueous solution. When the hydrophilic nature of the obtained hydrophilic polyvinylidene fluoride porous membrane was investigated like the work example 1, as shown in the 1st table, good hydrophilic nature was shown like the thing of a work example 1, and temporal deterioration was not seen, either.

The hydrophilic polyvinylidene fluoride porous membrane was obtained like the work example 1 except replacing with a work-example 70.5 w/v% polyvinyl pyrrolidone aqueous solution, and using a 1 w/v% cane sugar aqueous solution. When the hydrophilic nature of the obtained hydrophilic polyvinylidene fluoride porous membrane was investigated like the work example 1, as shown in the 1st table, good hydrophilic nature was shown like the thing of a work example 1, and temporal deterioration was not seen, either.

The hydrophilic polyvinylidene fluoride porous membrane was obtained like the work example 1 except replacing with a work-example 80.5 w/v% polyvinyl pyrrolidone aqueous solution, and using a 1 w/v% aspartic acid aqueous solution. When the hydrophilic nature of the obtained hydrophilic polyvinylidene fluoride porous membrane was investigated like the work example 1, as shown in the 1st table, good hydrophilic nature was shown like the thing of a work example 1, and temporal deterioration was not seen, either.

The hydrophilic polyvinylidene fluoride porous membrane was obtained like the work example 1 except replacing with a work-example 90.5 w/v% polyvinyl pyrrolidone aqueous solution, and using a 1 w/v% glutathione aqueous solution. When the hydrophilic nature of the obtained hydrophilic polyvinylidene fluoride porous membrane was investigated like the work example 1, as shown in the 1st table, good hydrophilic nature was shown like the thing of a work example 1, and temporal deterioration was not seen, either.

Although the compound which processes with the compound solution which has a hydrophilic group like work examples 4-9, and has a hydrophilic group was made to adsorb and being tried as like, without processing with the strong alkali solution which creates a hydrophobic polyvinylidene fluoride porous membrane like seven to comparative example 12 work example 1, and contains an oxidizing agent after that The compound which has a hydrophilic group was not adsorbed, and as shown in the 1st table, it was not able to give hydrophilic nature to a porous membrane.

第　1　表

	親水基を有する化合物	親水性*1			
				1カ月放置後	
		蒸留水	30w/v%ブドウ糖水溶液	蒸留水	30w/v%ブドウ糖水溶液
実施例 1	ポリビニルピロリドン(Mw40,000)	+	+	+	+
〃 2	ヒドロキシプロピルセルロース(6.0～10.0cps)*2	+	+	+	+
〃 3	ポリエチレングリコール(Mw20,000)	+	+	+	+
比較例 1	—	+	−	±	測定せず
〃 2	ポリビニルピロリドン(Mw40,000)	—	−	測定せず	〃
〃 3	ヒドロキシプロピルセルロース(6.0～10.0cps)*2	—	−	〃	〃
〃 4	ポリエチレングリコール(Mw20,000)	−	−	〃	〃
〃 5	—	+	−	〃	〃
実施例 4	ポリオキシエチレン　ポリオキシプロピレン共重合体	+	+	+	+
〃 5	グリセリン	+	+	+	+
〃 6	ブドウ糖	+	+	+	+
〃 7	ショ糖	+	+	+	+
〃 8	アスパラギン酸	+	+	+	+
〃 9	グルタチオン	+	+	+	+
比較例 7	ポリオキシエチレン　ポリオキシプロピレン共重合体	−	−	測定せず	測定せず
〃 8	グリセリン	−	−	〃	〃
〃 9	ブドウ糖	−	−	〃	〃
〃 10	ショ糖	−	−	〃	〃
〃 11	アスパラギン酸	−	−	〃	〃
〃 12	グルタチオン	−	−	〃	〃

＊1…水滴を膜上に滴下した際、20秒以内に細孔部に侵入して他方の面まで濡れた場合を(＋)とし、20秒以内に細孔部が濡れたものを(±)、20秒経っても濡れなかったものを(−)とした。

＊2…分子量のかわりに20℃　2w/v%水溶液の粘度で重合度を表示

(EFFECT OF THE INVENTION)

As stated above, invention creates the porous membrane which consists of polyvinylidene fluoride. After infiltrating a basin system solvent into the pore part of this porous membrane, a chemical treatment is carried out in the strong alkali solution containing an oxidizing agent. It is the manufacture method of the hydrophilic polyvinylidene fluoride porous membrane characterized by furthermore immersing this porous membrane into the compound solution which has a hydrophilic group. In order to oxidize in an instant by operation of the oxidizing agent intermingled in the double bond first generated on the polyvinylidene fluoride molecule by operation of strong alkali, to introduce a polar group and to form a hydrophilization layer, The surface which can stick to the compound which there is no possibility of producing a superfluous double bond, and can obtain the high porous membrane of the commodity value which has the outstanding white appearance of being, carrying out and assuming colorlessness, in a dry state, and has a hydrophilic

group is formed. It is what enables grant of hydrophilic nature with the compound which has the hydrophilic group which can give the hydrophilic nature which does not have temporal change highly. The hydrophilic nature temporally stabilized while high hydrophilic nature was shown, since hydrophilic nature was given by the compound which has the hydrophilic group which stuck to the pore surface is shown. Enjoy the outstanding character which the polyvinylidene fluoride porous membrane which is a base material since hydrophilization only of the pore surface is carried out has, and And chemical resistance, gamma ray-proof nature, The hydrophilic polyvinylidene fluoride porous membrane which was said when it came to what was excellent in safety and which has the outstanding character can be manufactured with sufficient operativity in an easy manufacturing process in a short time, and equipment cost and manufacture cost can also be made inexpensive. If the aqueous solution which dissolves potassium permanganate as an oxidizing agent, and dissolves potassium hydroxide or sodium hydroxide as a strong alkali solution is furthermore used in the manufacture method of this invention It is low cost and the more excellent hydrophilic polyvinylidene fluoride porous membrane can be obtained easily.

[Translation done.]